RECOVERY OF DILUTE ACETIC ACID VIA ESTERIFICATION REACTION CATALYZED BY AMBERLYST 15

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NOMENCLATURE

AA	acetic acid
C_i	concentration of species I ($mol/m^2.s$)
Ct	vacant site
E	process efficiency (%)
Ea	activation energy (cal/gmol)
ER	eley-rideal
FID	flame ionization detector
GC	gas chromatograpgy
k	specific reaction rate (constant)
K_C	catalysed reaction rate constant ($m^3/mol^{-1}g_{cat}^{-1}s^{-1}$)
Ke	equilibrium constant (dimensionless)
K_i	adsorption equilibrium constant for species *i*
LHHW	langmuir-hinshelwood-hougen-watson
	number of moles of A initially (entering)
PH	pseudo-homogeneous
X	conversion of key constant, A
Θ*i*	ratio of the number of moles of species *i* initially (entering) to the number of moles of A initially (entering)

PENUKARAN ASID ASETIK CAIR MELALUI PROSES PENGEKSTRAKAN DENGAN PEMANGKIN AMBERLYST 15

ABSTRAK

Proses pemulihan asid asetik daripada larutan akueus adalah masalah utama dalam bidang petrokimia dan industri kimia. Proses konvensional pemisahan fizikal seperti penyulingan dan pengekstrakan mengalami beberapa kelemahan. Dalam kerja ini, tindak balas pengesteran asid asetik dengan 2-etil-1-hexanol telah dikaji dalam kehadiran pertukaran ion resin Amberlyst 15. Kesan parameter operasi penting seperti suhu dan kelajuan pergolakan telah diperiksakan. Dalam lingkungan kajian, penukaran maksimum asid asetik mencapai 98.8% pada suhu 100 °C. Untuk kelajuan pergolakan, tiada kesan banyak untuk penukaran asid asetik dari 300rpm untuk 600pm dimana penukaran tertinggi asid asetik adalah 75%. Eksperimen data kinetik tindak balas pengesteran telah dikaitkan dengan pseudo-homogen (PH), Langmuir-Hinserlwood-Hougen-Watson (LHHW) dan Eley-Rideal (ER) model. Model LHHW memberikan keputusan yang terbaik dengan data esperimen. Tenaga pengaktifan bagi tindak balas ini telah ditemui sebanyak 71,08 kJ mol-^{1}.

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ABSTRACT

The recovery of acetic acid from its dilute aqueous solutions is a major problem in both petrochemical and fine chemical industries. The conventional physical separations such as distillation and extraction suffer from several drawbacks. In the present work, the esterification reaction of dilute acetic acid with 2-ethyl-1-hexanol has been studied in the presence of ion-exchange resin Amberlyst 15. The effect of important operating parameters such as speed of agitation and reaction temperature has been examined. Within the range of study, the maximum conversion of acetic acid reached 98.8% at temperature of 100 ℃. For speed of agitation, there is no much effect to the conversion of acetic acid ranging from 300rpm to 600pm where the highest conversion of acetic acid was 75%. Experimental kinetic data of the esterification reaction were correlated with the pseudo-homogeneous (PH), Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (ER) models. The LHHW model gave the best agreement with the data. The activation energy for the reaction was found to be 71.08 $kJmol^{-1}$.

CHAPTER 1

INTRODUCTION

1.1 Background of the Proposed Study

Aqueous solutions of acetic acid are produced as by-products or waste streams of many important chemical processes. A large amount of acetic acid containing waste is produced if the reaction is involving with acetic anhydride as well as in the production of cellulose esters, terephthalic acid and dimethyl terephthalate (Bianchi et al., 2002). The waste containing acetic acid is a major issue for those petrochemical and fine chemical industries in term of disposal. From the past, the waste containing acetic acid was sent to incinerator which is commonly practiced by industries. Nevertheless, it is not environmental friendly. Carbon dioxide and other hazardous compounds are released from incineration process and cause the pollution issues.

Several methods or patents have been proposed and published by researchers to recover the acetic acid. The methods include extraction, distillation, pervaporation, ion exchange, membrane separation and so forth. These methods are not promising due to some drawbacks in issue of economic (Ragaini et al., 2005). Apart from that, further treatments and some technical limits are the factors for the conventional methods which are being rejected. In view of these constraints, it is necessary the researchers to explore more alternative methods to replace the current methods in the recovery of acetic acid from waste stream.

In the present work, dilute acetic acid (20% w/w) was recovered using esterification method. The dilute acetic acid was reacted with 2-ethyl-1-hexanol to produce 2-ethyl-1-hexyl acetate as main product.

1.2 Research Objectives

The research objectives of the research study are:

i) The effect of important parameters such as temperature and speed of agitation were examined.

ii) The kinetic model was developed based on the data obtained from experiment.

1.3 Scope of Proposed Study

The scope of the present study focused on the conversion of acetic acid in a wastewater to a more valuable ester product via esterification process. Effect of the important of operating parameters on the process was studied. The range of operating parameters for temperature and speed of agitation were varied from 70℃ to 100℃ and 300rpm to 600rpm respectively. In kinetic model part, the experimental data was fitted with the suitable kinetic model such as Pseudo-homogeneous model (PH), Langmuir-Hinshelwood-Watson model (LHHW) and Eley-Rideal model (ER).

1.4 Significance of Proposed Study

In esterification reaction, carboxylic acid reacts with alcohol to produce ester and water. In the present work, 2-ethyl-1-hexyl acetate is produced via this reaction. 2-ethyl-1-hexyl acetate has a good market value as raw materials for the sunscreen cream and anti-aging cream (Ragaini et al., 2005).

Incineration has been widely applied by the industries for the past since it was a cheap, easy operation, and a common method to remove the acetic acid from waste stream. By adopting this method, large amount of carbon dioxide gaseous will be produced from the incineration of hydrocarbon compounds to the atmosphere. Thus, the issue of air pollution is concerned. The method of recovery of acetic acid via esterification reaction is more environmental friendly and worth to be explored.

CHAPTER 2

LITERATURE REVIEW

This review of literature is about the recovery methodologies of the acetic acid from wastewater, reactant used, type of catalyst, and kinetic models for esterification of wastewater containing acetic acid with alcohol.

2.1 Recovery Methodology

Extraction, distillation, pervaporation, esterification, membrane separation and reactive distillation are the example methods proposed to recover the acetic acid from waste stream. In fact of conventional physical separation methods, extraction and distillation show several drawbacks.

An application of reactive extraction has been applied to recover the acetic acid from aqueous pyrolysis oil. Rasrendra et al., (2011) shows that 84% of acetic acid

recovery was achieved at equilibrium condition (room temperature) by selecting proper amine and diluents combination. Apart from that, more than 80% of acetic acid is recovered in term of efficiency with less energy requirement has been proven by Katikaneni & Cheryan, (2002) and Mahfud et al., (2008). Although this method has high recovery efficiency rate, but further treatment is required. Some significant efforts have been contributed for looking other suitable alternatives to recover acetic acid.

Bipolar membrane electrolysis is one of the methods that less researchers would like to adopt to recovery the acetic acid from dilute wastewater. Yu et al., (2000) claimed that 0.2% (wt%) of acetic acid was recovered quite successfully with up to 70% of conversion. Unfortunately, recovery of acetic acid by using membrane is always a costly technology to the industry. Azeotropic distillation is a quite interesting method to be adopted to recovery the acetic acid from waste stream, but it generates the environmental issues (Gualy et al., 1996).

Esterification is one of the popular methods that often practiced by researches to recovery the acetic acid from wastewater. Jermy & Randurangan., (2005) had carried out esterification reaction by recovering the acetic acid using n-butyl alcohol. The experiment was studied over various type of protonated AL-MCM-41 with different Si/Al ratio. Furthermore, several kinetic studies had been done by recovering the acetic acid through esterification reaction. Robert et al., (1997) and Blagov et al., (2005) both had developed their kinetic model by fitting the experimental data via esterification. The reaction was carried out by using methanol in the presence of hydrogen iodide. In the

present work, the esterification reaction was carried out to recover the acetic acid by reacting with 2-ethyl-1-hexanol over the Amberlyst 15 (dry).

2.2 Catalyst

In esterification reaction, catalyst is usually used in the process. There are three common types of catalyst used in the reaction. They are homogeneous catalyst, heterogeneous catalyst and enzyme. The function of the catalyst is providing alternative path by lowering the activation energy required for the reaction. In industry, the mineral liquid acids are widely applied in the past for esterification such as sulphuric acid and *p*-toluenesuphonic. By using these homogeneous catalysts, the catalytic activity and yield of the acetic acid are high (Peters et al., 2005). However, these acid catalysts are found to be toxic, corrosive, and the catalysts cannot be easily separated from the product mixture (Teo & Saha, 2004; Akbay et al, 2011; Lilja et al., 2002). Furthermore, Shaojun & Brent., (2010) claimed that the neutralization and separation step are required to neutralise and remove the homogenous catalyst from the product mixture.

Due to the several disadvantages of homogeneous catalysts, the ion-exchange resin is become an attractive alternative catalyst. The ion-exchange resin may be Amberlyst 15, Dowex 50W, Smopex 101, Nb_2O_5, Sulphated ZrO_2, and so forth. The ion-exchange resins are not corrosive, has long activity life and easily to be separated from the product mixture (Altiokka & Citak., 2002; Toor et al., 2011). Some researchers have compared the process efficiency (*E* %) among the homogeneous catalyst and

heterogeneous catalyst. Bianchi et al., (2002) has done the process efficiency (*E* %) comparison between homogeneous and heterogeneous catalysts for the esterification of acetic acid and 2-ethyl-1-hexanol. Their research findings are shown in Table 2.1.

Table 2.1 Process Efficiency Comparison between Homogeneous and Heterogeneous Catalysts

Catalyst used	E %
H_2SO_4	69.2
Nafion NR 50	45.6
Amberlist 15	44.7
Amberlist 200	43.6
Amberlist IR 120	42.6
SO_4 – Zirconia	31.9

From the Table 2.1, sulphuric acid gives the highest percentage of process efficiency. Unfortunately, sulphuric acid is not easily to be removed from the product mixture as stated above. Another paper has examined a comparison of commercial solid acid catalysts for esterification (Peters et al., 2005) and their findings are shown in Table 2.2.

Table 2.2 The Activity of the Different Heterogeneous Catalyst Used in the Esterification Reaction

The K_C value shown by using different heterogeneous catalyst in the esterification reaction between acetic acid and butanol at 75 ℃.		
Catalyst	Amount (g)	K_C (m^3 mol^{-1} g_{cat}^{-1} s^{-1})
Amberlyst 15	1.90	1.6×10^{-8}
Smopex-101	1.85	2.4×10^{-8}
H-USY-20	2.88	9.8×10^{-10}
H-ZSM-5-12.5	2.82	5.9×10^{-11}
H-BETA-12.5	2.81	7.7×10^{-10}
H-MOR-45	2.79	1.0×10^{-10}
ZrO2	5.00	8.8×10^{-9}
Nb_2O_5	5.07	9.8×10^{-11}

From the Table 2.2 Smopex-101 and Amberlyst 15 both gives the first and second highest number of Kc among the zeolites and ion-exchange resins. The amount Smopex-101 and Amberlyst 15 used in gram is only 1.85 and 1.90 respectively.

In the present work, Amberlyst 15 is chosen as heterogeneous catalyst for the esterification reaction of dilute acetic acid with 2-ethyl-1-hexanol. Saha & Sharma. (1995), Teser et al. (2009) and Peter et al. (2005) have provided the physical properties of Amberlyst 15. The physical properties include shape, size, porosity, temperature, acidity and so forth which are shown in Table 2.3.

Table 2.3 The Properties of Amberlyst 15

Physical Properties	Amberlyst 15
Shape	Bead
Size (mm; min 90%)	0.5
Internal Surface Area (m^2 / g)	55.0
Acidity (mequiv. / g)	4.7
Cross Link Density (% DVB)	20-25
Porosity (vol %)	36
Functional Group	Sulphonics
Matrix	Macroreticular copolymer styrene-DVB
Temperature Stability (K)	293

2.3 Reactants used

In the esterification reaction, carboxylic acid is reacted with alcohol to produce ester and water. Most of the published papers covered the esterification of the concentrated acetic acid. Only few of the papers have discussed about dilute acetic acid.

In the chemical process, there are some dilute acetic acid are produce as a by-product. 35% (w/w) aqueous solution of acetic acid was produce from the manufacture of cellulose acetate from acetylation of cellulose. Furthermore, the dilute acetic acid (5-20% w/w) has also being produced from the process of synthesis of glyoxal acetaldehyde and nitric acid (Teo & Saha., 2004). Therefore, an esterification reaction between acetic acid and *n*-butanol / *iso*-amyl alcohol was investigated in a reactive distillation column by using microporous ion-exchange resin, Indion 130. The reactions

were found to be equilibrium limited (Saha et al., 2000). Esterification of acetic acid with various alcohols such as *n*-butyl alcohol, isobutyl alcohol and tertiary butyl alcohol has been studied in the presence of Mesoporous Al-MCM-41 molecular sieves as heterogeneous catalyst. From the observation, the *n*-butyl alcohol conversion was found to be higher than isobutyl alcohol and tertiary butyl alcohol (Jermy & Pandurangan., 2005).

Kirumakki et al., (2005) have reported that the degree of liquid phase esterification on the type of alcohols and the acidity of the zeolites. This research has been done on the liquid phase esterification of *n*-propyl, *n*-butyl, *iso*-propyl and *iso*-butyl alcohols on acetic acid over the various zeolite types of Hβ, HY and HZSM5. In the present work, 2-ethyl-1hexanol will be served as one of the reactants to be reacting with acetic acid. There are not many researchers study the esterification reaction using 2-ethyl-1-hexanol. Ragaini et al., (2005) claimed that the reaction took place in the organic phase and the conversion of acetic acid reached 70%. Besides, kinetic model was performed. The result brought to the hypothesis that the diffusion of the reagents and products in and out the catalyst pores is not a rate-determining step. Table 2.4 shows the several reactants that have been used to produce different acetate ester.

Table 2.4 The Summary of Common Alcohol Reactants Used for Esterification reaction

References	Reactant used
Bianchi et al., (2003)	*n*-butanol, 2-ethyl-1-hexanol
Dash & Parida., (2006)	*n*-butanol
Jazi (2010)	Benzyl Alcohol
Hasanoglu et al., (2009)	Ethanol
Kirumakki et al., (2005)	*n*-propyl, *n*-butyl, *iso*-propyl, *iso*-butyl

2.4 Kinetics Model

In Gangadwala et al., (2003) research, the esterification reaction was conducted in the presence of the ion-exchange resin Amberlyst 15. This heterogeneous kinetics model including Pseudo-Homogeneous (PH), Eley-Rideal (ER) and Langmuir-Hinshelwood-Hougen-Watson (LHHW) were applied to correlate kinetics data available for different operating parameters. For the ER model, the esterification reaction was assumed that the adsorbed butanol and acetic acid species on the catalyst surface are taken places. But for LHHW model, all of the components were assumed in their adsorbed phases. Teo & Saha., (2004) stated that, the model with the least sum of squares and random residuals would be the most suitable from the statistical standpoint. The researchers claimed that the LHHW model is applicable when the rate determining step is the surface reaction between adsorbed molecules. For ER model, it is applicable if the rate limiting step is surface reaction where it takes place between one adsorbed species and one non-adsorbed reactant from the bulk liquid phase.

In the published papers, the most common models that have been developed by researchers are Pseudo-Homogeneous (PH), Eley-Rideal (ER) and Langmuir-Hinshelwood-Hougen-Watson (LHHW). This kind of kinetics model is only applied to heterogeneous reaction. Gangadwala et al., (2003) stated that the LHHW models explain the data successfully over a wide range of catalyst loading and temperature for esterification reaction under the reaction between acetic acid and n-butanol. Apart from that, ER and LHHW model yielded a better result under the reaction between acetic acid and methanol catalyzed by amberlyst 36 among IQH, the NIQH, the ER, and the LHHW models (Tsai et al., 2011). Altiokka & Citak (2002) stated that ER model is suitable the reaction has been found to occur between an adsorbed alcohol molecule and a molecule of acid in the bulk phase under the reaction between acetic acid and isobutanol catalyzed by strong acidic ion-exchange acid.

Based on the review, LHHW model is prefer compare to the other two models. In most of the papers, LHHW model gives the best representation of kinetic behavior for all practical purposes under a given condition and explain the data successfully over a wide range of temperature for esterification reaction.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Research Design

This study focuses on the conversion of dilute acetic acid via esterification process. In a batch reactor by varying the temperature and speed of the concentration of the samples was analyzed by gas chromatography using flame ionization detector. The details procedure for the execution is shown in the subsequent section.